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ORIGINAL PAPER

Development of platinum-free catalyst and catalyst with low platinum content for cathodic oxygen reduction in acidic electrolytes

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Abstract Studies are presented of the kinetics and mechanism of oxygen electroreduction on CoPd catalysts synthesized on XC 72 carbon black. As shown both in model conditions and in tests with the cathodes of hydrogen–oxygen fuel cells with proton conducting electrolyte, the CoPd/C system features higher activity as compared to Co/C. It is found by means of structural analysis that CoPd alloy is formed in the course of the catalyst synthesis. This provides the higher catalytic activity of the binary systems. CoPd/C catalyst is also more stable in respect to corrosion than Pd on carbon black. Measurements on a rotating ring–disc electrode show that the CoPd/C system provides preferential oxygen reduction to water in the practically important range of potentials ($E > 0.7$ V). The similarity of the kinetic parameters of the oxygen reduction reaction on CoPd/C and Pt/C catalysts points to a similar reaction mechanism. The slow step of the reaction is the addition of the first electron to the adsorbed and previously protonated O_2 molecule. Studies of the most active catalyst in the fuel cell cathodes are performed.

Binary PtCo catalysts (metal atomic ratio of 1 : 1) with low platinum content (7.3 wt.%) modified by phosphorus or sulfur are developed and studied. It is demonstrated that the specific activity of the PtCoS/C (Pt : S = 1 : 1) catalytic system for the O_2 reduction reaction exceeds that of a commercial Pt/C catalyst (E-TEK). The tolerance of the catalyst modified with sulfur is at least six times higher than that of Pt/C (E-TEK).

Keywords Kinetics · Oxygen electroreduction · CoPd catalysts · Specific activity · Tolerance · Selectivity

1 Introduction

Cathodic oxygen reduction is in many respects the key reaction for low-temperature hydrogen– and methanol–air fuel cells (FC) with a polymer proton–conducting electrolyte. The most active electrocatalysts for this reaction are the PtM systems, where M = Co, Ni, Fe, Cr [1–3]. Considerable efforts [4–6] on the development of Pt alternatives without using Pt group metals brought no success, as the characteristics of these catalysts are essentially lower than those of Pt.

In our opinion, a more realistic way of Pt replacement for a whole range of low-temperature FC applications is the employment of Pd–based electrocatalysts that are four times cheaper, as compared to Pt.

Pd is close to Pt in its electronic structure, but its activity for the oxygen reaction is relatively low and its corrosion stability is insufficient. We assumed that these drawbacks might be largely removed by synthesizing binary Pd–base metal (Co, Ni, Fe, Cr) systems. As shown in the literature, other groups have also worked in this direction [7–9]. However, unlike these works that were conducted with compact (film) electrodes, we set ourselves the task of developing highly dispersed nanosize systems, of which the characteristics could be studied not only in model conditions, but also in FC prototypes. In order to solve the above problem, we developed an original high-temperature

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method of PdCo binary system synthesis on the basis of organic precursors.

Another task was the development of methods of PtCo cathodic catalyst modification in order to increase its tolerance towards methanol while preserving its activity for cathodic oxygen reduction. The main direction chosen was sulfur and phosphorus introduction using organic complexes. The use of chalcogens, particularly sulfur, for Pt/C modification results in an increase in catalyst tolerance towards methanol [10].

2 Experimental

2.1 Catalyst synthesis

2.1.1 *Synthesis of PdCo/C catalysts*

The basic synthesis method was a high-temperature thermochemical route in which cobalt organic precursors were used. Catalysts containing Co and Pd applied to XC 72 carbon black (Vulcan) were prepared using Co tetra(*p*-methoxyphenyl)porphyrin (CoTMPP) or Co phthalocyanine (CoPc) (Aldrich) and Pd chloride (PC "AURAT"). Carbon black was previously heated for an hour in argon at 600 °C. The specific surface area of the treated carbon black was 250 $m^2 g^{-1}$. As shown earlier [11], the optimum activity in acidic solutions is achieved by applying three monolayers of one of the N_4–complexes onto the carbon black surface. In the case of XC 72 carbon black, this corresponds to about 30 wt.% of the initial complex. The necessary amount of N_4-complex and $PdCl_2$ was introduced into the mixture of ethanol and chloroform (KHIMMED, Russia), subjected to ultrasonic treatment, applied to carbon black, dried until complete removal of solvents and subjected to pyrolysis for 1 h in argon at 800 °C. It was assumed that Co nanoparticles formed in the pyrolysis would hinder the agglomeration of the dispersed Pd particles and provide alloy formation. The initial Pd content was 25–95 at.% in respect to cobalt, the amount of which, in all cases, corresponded to 30 wt.% of CoTMPP (CoPc) in the system of carbon black and CoTMPP, as discussed above. Therefore, an increase in overall content of metals applied to carbon black was observed due to the increase in the initial Pd content.

2.1.2 *PtCo/C system modification with phosphorus or sulfur*

Earlier, PtCo (1 : 1) catalyst (7.3 wt.% Pt, supported on XC 72) was synthesized using the high–temperature method [12]. The PtCo/C system was modified by phosphorus and sulfur. Phosphorus was introduced using its organic compounds (triphenylphosphine oxide ($C_{18}H_{15}PO$), ethylbutyldiphenylphosphonium hexafluorophosphate ($C_{18}H_{24}P_2F_6$)) or red phosphorus. Modification with sulfur was achieved using thiourea. The catalyst synthesis was performed by means of the high–temperature method after evaporating the solution of the required amounts of components in a water–alcohol mixture (XC 72 carbon black, H_2PtCl_6, Co N_4-complex and sulfur or phosphorus precursor). The atomic ratio of components in the catalytic systems was: Pt/Co – (1 : 1), Pt/P – (20 : 1); when introducing sulfur, the Pt/S ratio was varied from 1 : 0.5 to 1 : 2.

2.2 Structural research methods

Structural and morphological studies of the PdCo/C system were performed using XPS, XRD and TEM methods and on the basis of CO adsorption. The measurements by XPS were carried out with a VGESCA 3MKP spectrometer. The intensities and energies of X-ray bands were analyzed for the core levels of Pd 3d, Co 2p, C 1s, O 1s, S 2p. The relative concentrations of the elements were determined according to the model of homogeneous solid solution.

X-ray studies were performed with a JDX-15PA JEOL diffractometer. The diffraction spectra were recorded in the angle range $15° \le \theta \le 100°$. The structural and morphological parameters of the catalyst particles were determined using EM-301 "Philips" and EM-400T electron microscopes at an accelerating voltage of 80 keV at the high-resolution stage of 1.8 Å.

2.3 Preparation of electrodes and electrochemical research methods

Electrocatalytic activity was measured using a rotating disc (RDE) and rotating ring–disc electrodes (RRDE) in 0.5 M H_2SO_4 (bidistilled water and sulfuric acid of special grade (KHIMMED, Russia)). The materials for the electrode preparation were as follows: Nafion (5% solution in a mixture of low–molecular aliphatic alcohols, Aldrich); 96.6% ethanol (KHIMMED, Russia). The RDE disc was made of pyrographite; its surface area was 0.2 cm^2. In the RDE measurements, an extremely thin catalyst layer (100 $\mu g\ cm^{-2}$) was deposited onto the disc. The catalyst thickness layer was ~2.5–3.0 μm. In order to prepare catalytic ink, a catalytic mixture (2 mg of the test catalyst, 0.5 mL of ethanol and 0.7 μL of 5% Nafion solution) was subjected to ultrasonic treatment, after which its aliquot was applied to the disc and dried in air. In the case of RRDE (a demountable electrode), the disc was prepared as described above, and the Pt ring electrode was previously platinated and activated, after which the whole electrode was mounted. The potential at the ring was always 1.2 V. The efficiency coefficient of transport from the disc to the ring (*N*) was determined by means of two methods: on the basis of geometric parameters of the disc and ring and experimentally in 0.1 M NaOH solution with $K_3Fe(CN)_6$. The experimentally determined value of the coefficient *N* was 0.41 ± 0.02, while the calculated value was 0.38. In further analysis of the experimental data, the *N* value was assumed to be equal to 0.4. Detail of the RRDE measurements is given elsewhere [13].

The specific surface areas of the catalysts were determined on the basis of hydrogen and CO desorption voltammograms obtained at a disc electrode with a thin catalyst layer [14].

2.4 Study of catalyst corrosion stability

This technique consisted in continuous catalyst (50 mg) treatment with 0.5 M H_2SO_4 (50 mL) while bubbling air through the solution and periodic temperature increase to 60 °C. The overall treatment time was varied and was as high as 350 h. After treatment, the catalyst specific surface area of the metal phase was determined from CO desorption. The electrocatalytic activity after corrosion treatment of different durations was found from model experiments at the RDE and within the cathode of a methanol–oxygen FC with proton–conducting electrolyte.

2.5 Tests of bimetallic catalysts within active layers of membrane electrode assemblies

Tests of methanol–oxygen and hydrogen–air FC were performed at the ElectroChem. Inc and Arbin Instrument test boards with 5 cm^2 electrodes using Nafion as polymer electrolyte. Membrane Electrode Assemblies (MEA) were based on Nafion 117 membranes. TORAY 090 and 060 paper was used as a gas-diffusion layer (GDL). A dynamic hydrogen reference electrode allowed obtaining polarization curves for separate electrodes within the FC.

2.5.1 Methanol–oxygen FC

The suspension of the catalyst with Nafion was applied to GDL by spraying. In all cases, 30 wt.% PtRu (1 : 1) (E-TEK) catalyst was used as anodic catalyst while cathodic catalysts were varied. The MEA was prepared by pressing at a temperature of 130 °C and a pressure of 70 kg cm^{-2}. 1 M methanol aqueous solution was circulated at 4–10 mL min^{-1}; oxygen consumption was 10–20 mL min^{-1} and the temperature was 50 °C.

2.5.2 Hydrogen–air FC

The mounting of the electrode assembly was performed by joint pressing of the cathode, Nafion 117 membrane and the anode at 150 kg cm^{-2} and 130 °C for 1 min. Catalyst suspension with Nafion content of 40 wt.% of dry substance was applied by pasting on GDL (TORAY 090 paper hydrophobized by 20 wt.% of Teflon). After drying, a small amount of Nafion solution was applied to the active layers, after which they were pressed onto the membrane (subjected to the standard treatment). The hydrogen pressure at 60 °C was 1 atm., while the air pressure was 2 atm. The temperatures of gas humidification and gas consumption were adjusted so as to eliminate hysteresis between the forward and reverse runs of the discharge curve.

Partial optimization of the cathode with PdCo/C catalyst was performed using 20 wt.% Pt (E-TEK) as the anode. A mixture of PdCo/C catalyst with 30 wt.% Nafion was placed onto Teflon treated paper. Anodes based on 20 wt.% Pt (E-TEK) were prepared in a similar way.

3 Results and discussion

3.1 Study of cathodic PdCo bimetallic system

Figure 1 and Table 1 compare data on oxygen reduction (ORR) for the Pt-free catalysts. The soluble admixtures were removed by acidic treatment prior to the electrochemical measurements. The polarization curves of Fig. 1

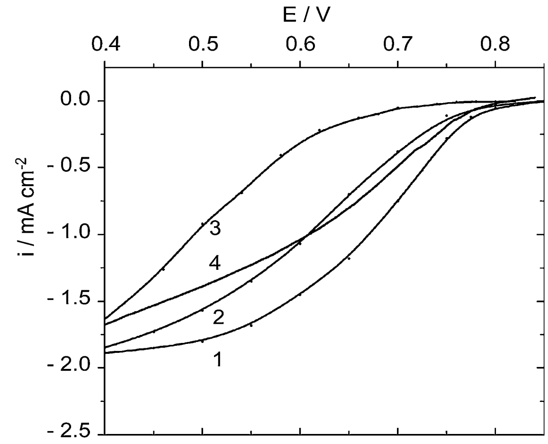


Fig. 1 Polarization curves at RDE in a 0.5 M H_2SO_4 with catalysts of: (1) XC 72 + CoTMPP + Pd (1 : 1); (2) XC 72 + CoTMPP; (3) XC 72 + CoPc; (4) XC 72 + CoPc + Pd (1 : 1). Electrode rotation rate, 680 rpm, scan rate, 1 mV s^{-1}, the oxygen atmosphere

Table 1 Values of steady-state potentials and current densities corrected according to the Levich–Koutecky equation for the binary systems obtained at RDE at m = 1,420 rpm at 20 °C; 0.5 M H_2SO_4, oxygen atmosphere, scan rate, 1.0 mV s^{-1}

Catalyst: XC 72 +	E_{st}/V (rhe)	i/mA mg_{cat}^{-1} at E/V	
		0.75	0.70
CoPc	0.80	1.6	4.0
CoPc + Pd (1 : 1)	0.92	6.3	11.0
CoTMPP	0.90	4.0	6.5
CoTMPP + Pd (1 : 1)	0.90	6.1	16.6

are the immediate data obtained at RDE with a thin catalyst layer. In Table 1, the data are compared at E = 0.75 and 0.70 V with the mass transport corrected mass-specific value (according to the Levich–Koutecky equation). The binary PdCo/C systems possess a higher electrocatalytic activity than Co/C in the case of pyropolymers based both on CoTMPP and CoPc. The catalyst based on CoTMPP with the highest activity was chosen as the basic bimetallic Pt-free system for detailed research.

3.1.1 *Structural studies of the PdCo/C system*

According to the literature, PdCo and PtCo alloys [1–5, 7–9] feature the highest activity in ORR as compared to monocatalysts. Structural studies of synthesized catalysts show that the chosen synthesis method results in alloy formation. According to XPS data [14], in the samples with initial PdCo content of 1 : 1 and 4 : 1 (atomic ratios) the position of the $Pd3d_{5/2}$ band corresponds to 335.4 eV and is shifted in the negative direction by 0.3 eV, as compared to the position of this band in Pd/C (Fig. 2a). On the basis of these data, the electronic density increases at Pd atoms. Such a shift of the maximum was observed in the case of PtCo/C alloy (Fig. 2b) [12]. The energy values of the components for the $Co2p_{3/2}$ band are 779.6, 780.6 and 782.4 eV. This corresponds to cobalt in the oxidized state and in the ligand environment of the modified nitrogen-enriched structure. According to XRD data, the PdCo/C system is characterized by a decrease in the Pd cubic lattice parameters. The characteristic parameter size of the metallic Pd cubic lattice is 0.3882 nm, while in the catalytic PdCo/C system the lattice parameter decreases to 0.3871 nm, which can be explained by cobalt dissolution in Pd and alloy formation. Some additional data on the composition of PdCo/C were obtained by studies of CO adsorption performed at Pd/C, Co/C and PdCo/C. It was shown [14] that an additional desorption maximum is observed in the case of PdCo/C, as compared to CO desorption maxima for Pd/C and Co/C due to CO desorption from the alloy surface.

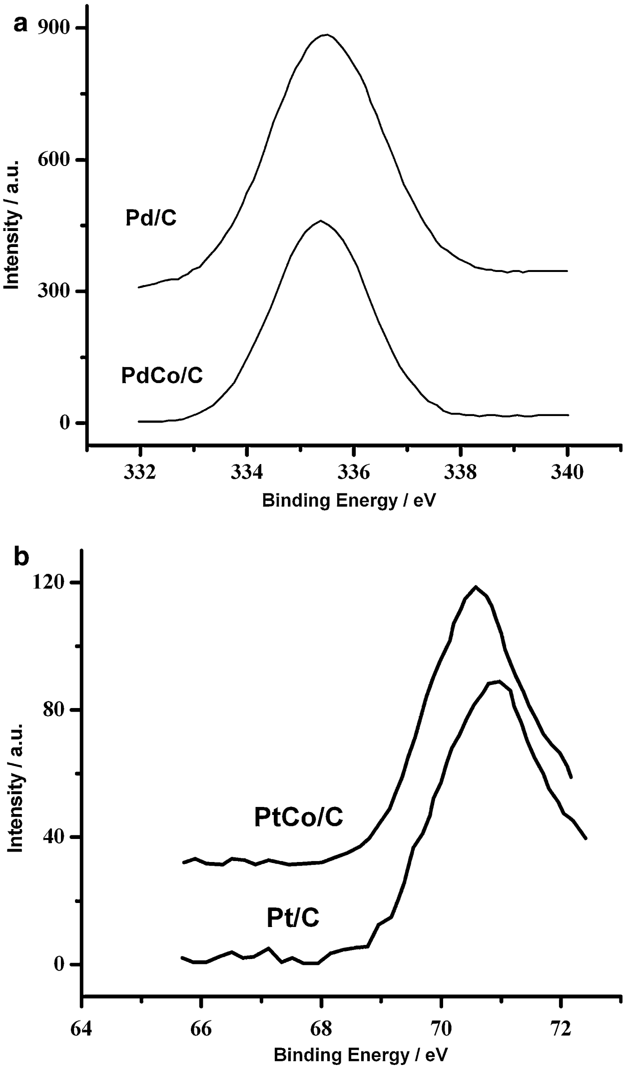


Fig. 2 (**a**) XPS spectra of Pd/C and PdCo/C catalyst. (**b**) XPS spectra of Pt/C and PtCo/C catalyst

According TEM data, the particle size distribution at the carbon support is sufficiently uniform for the metal phases of PdCo/C catalyst. The particle size distribution forms a wide spectrum with a maximum at 15–20 nm.

3.1.2 *Electrocatalytic characteristics of the PdCo/C system*

Table 2 shows the main kinetic parameters for ORR for PdCo/C. PdCo/C features a higher activity for the ORR as compared to Co/C. The value of steady-state potential (E_{st}) is ~0.90 V and the highest specific activity is observed for a Pd content from 50 to 80 at.%.

Figure 3 shows oxygen reduction polarization curves at RDE with 20 wt.% Pt (E–TEK) (curve 1) (similar characteristics were obtained in [15]) and at the most active

Table 2 Dependence of the catalyst activity on their composition in ORR (RDE)

Catalyst composition: XC 72 +			E_{st}/V (rhe)	$\partial E/\partial$logi/mV	i/mA mg^{-1}_{cat} at E = 0.70 V
Initial components	Metal content/wt.%	Pd : Co atomic ratio			
CoTMPP	3.2	–	0.83	70; 120	3.8
CoTMPP + $PdCl_2$	5.1	1 : 3	0.88	70; 120	10.0
CoTMPP + $PdCl_2$	9.0	1 : 1	0.88	70; 120	16.0
CoTMPP + $PdCl_2$	16.5	7 : 3	0.90	55; 130	10.0
CoTMPP + $PdCl_2$	26.4	4 : 1	0.90	64; 125	12.0
CoTMPP + $PdCl_2$	35.2	9 : 1	0.88	62; 125	4.2
CoTMPP + $PdCl_2$	53.0	9.5 : 0.5	0.85	64; 125	8.9

0.5 M H_2SO_4, 60 °C, oxygen atmosphere. Scan rate, 1.0 mV s^{-1}

PdCo/C catalyst (curve 3). As seen from Fig. 3 and also from Table 2, the polarization curve slope in the range of potentials from E_{st} to 0.70–0.65 V varies from 0.060–0.070 to 0.120–0.130 V. It is independent of the composition of the PdCo/C system and close to the polarization curve slope value for Pt/C. This is an important argument in favor of a similar ORR mechanism on PdCo/C and Pt/C. For Pt and other metal electrodes, the ORR mechanism in acidic solutions is discussed in detail elsewhere [16–18]. The presence of the curve region with slope 0.120 V suggests a slow reaction step of electron addition to the adsorbed and previously protonated O_2 molecule. With positive potential shift, surface coverage by O_2 molecules decreases due to the appearance of oxygen-containing particles adsorbed from water and hindering the adsorption of molecular oxygen. This results in a reaction rate decrease with increase in potential, which is demonstrated by the appearance of a region of 0.060 V slope. Possible variants for describing the reaction within the terms of formal electrochemical kinetics are provided elsewhere [16, 18, 19]. Taking into account that in the case of PdCo/C catalyst the Tafel curve of slope of 0.060 V corresponds to a wider range of potentials, as compared to Pt/C catalyst, it can be assumed that oxygen-containing particles are adsorbed on PdCo/C at less positive potentials and the decrease in the reaction rate and decrease in slope from 0.120 to 0.060 V is observed at a more negative potential as compared to Pt/C. This discrepancy is caused by the different electronic structure of the catalyst metal components. As seen in Fig. 3, this results in the specific activity of the most promising PdCo catalyst being lower by seven (slope range about 0.120 V) to 15 times (slope range about 0.060 V) than the activity of Pt/C catalyst. One should take into account that the specific surface area of Pt/C (65 m^2 g^{-1} for 20 wt.% Pt (E–TEK) [15]) exceeds that of PdCo at the same carbon support (about 35–45 m^2 g^{-1}).

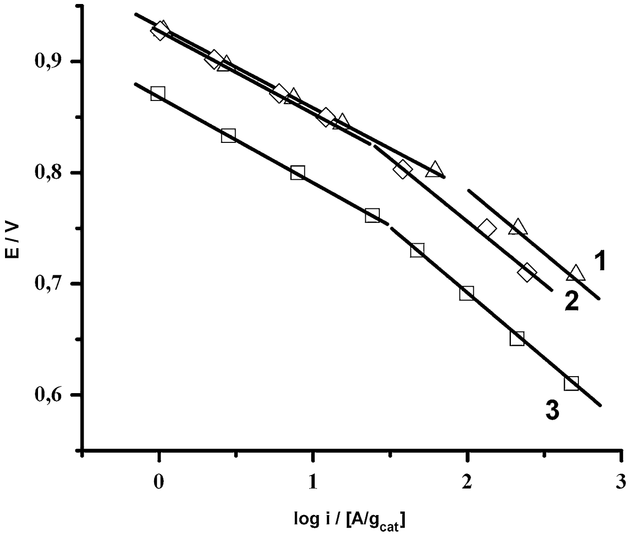


Fig. 3 Tafel curves of oxygen reduction at RDE coated by a thin catalyst layer (100 µg cm^{-2}): (1) 20% Pt (E-TEK); (2) CoTMPP + 7.3% Pt (Pt : Co = 1 : 1); (3) CoTMPP + Pd (Pd : Co = 1 : 1) The electrode rotation rate is 1,480 rpm; scan rate, 5 mV s^{-1}. 0.5 M H_2SO_4, the oxygen atmosphere; 60 °C

Calculations of the ratio of the rate constants for direct reaction to water (k_1) and for oxygen reduction to hydrogen peroxide (k_2), were performed according to the equation [20]

$$I_D N/I_R = 1 + 2k_1/k_2 + 1/Z_{H_2O_2}[k_3 + (k_3 + k_4)(1 + 2k_1/k_2)]\omega^{-1/2} \quad (1)$$

where N is the coefficient of the effective product transport from the disc to the ring, ω is the angular electrode rotation rate, k_3 is the rate constant of the further H_2O_2 transition and k_4 is the rate constant of the catalytic decomposition of hydrogen peroxide, $Z_{H_2O_2} = 0.62\,D_{H_2O_2}\nu^{1/6}$. In $I_D N/I_R$ versus $\omega^{-1/2}$-coordinates, Eq. 1 corresponds to a straight line with an intercept on the $I_D N/I_R$ axis of $A = 1 + 2k_1/k_2$. The value of intercept A characterizes the ratio of the rates of two- and four-electron processes of oxygen reduction.

It was shown [14], that the amount of H_2O_2 formed at the disc electrode at $E_D > 0.7$ V does not exceed 5–7 µA for all catalysts presented in Table 3. This does not allow quantitative calculation of the k_1/k_2 ratio to be performed in this range of potentials, but shows a sufficiently high rate of oxygen reduction to water. At $E = 0.60–0.30$ V the value of the k_1/k_2 ratio for PdCo/C is higher than that of Co/C, but is considerably inferior to that of Pt/C. Thus, the data obtained by the RRDE method demonstrate that PdCo/C provides predominant selective oxygen electroreduction via the four-electron route.

3.1.3 *Results of corrosion tests*

The corrosion stability of electrocatalysts is their most important characteristic, particularly in the case when they contain Pd, as its stability is considerably lower than that of Pt. However, Pt is dissolved in model conditions and during FC testing [12, 21], which results in a decrease in performance and membrane degradation.

Some data are presented in Fig. 4. The initial brief acidic treatment results in a considerable decrease in specific activity and specific surface area, which can be explained by dissolution of non-alloyed Pd. Further increase in treatment time does not noticeably affect the metal surface area. Comparison of the activity of cathodic catalysts in the studied range of acidic treatment times demonstrates that the parameters are changed in the same way both in model conditions and within FC.

3.2 Comparison of characteristics of PdCo/C and PtCo/C systems in ORR

Figure 3 compares Tafel curves measured at RDE at various catalysts. The coincidence of curves 1 (Pt/C, 20%Pt) and 2 (PtCo/C, 7.3% Pt) in the range of Tafel slope of ~0.060 V shows similar specific activity per catalyst mass. The specific activity per platinum mass is higher for PtCo/C as compared to Pt/C. PdCo/C catalyst features a lower activity as compared with Pt-containing catalysts (curve 3).

Table 3 Values of steady-state potentials (E_{st}) at the disc electrode, oxidation current of H_2O_2 at the ring electrode (I_R), and values of k_1/k_2 ratio for various catalysts

Catalyst: XC 72 +	E_{st}/V (rhe)	I_R/μA at E_D/V		k_1/k_2 at E_D/V	
		0.75	0.20	0.60	0.30
Co, 3.2 wt.%	0.90	7	80	2.2	0.15
PdCo (1 : 1), 9 wt.%	0.89	5	60	4.6	0.95
Pt, 20 wt.%	1.00	2.0	10	$\gg 1$	31.0

0.5 M H_2SO_4, 20 °C

In order to develop further studies of cathodic catalysts based on Pd, it is important to compare structural characteristics of the PtCo and PdCo systems. The employment of the high–temperature synthesis method and application of Co precursors when choosing the optimum Pt(Pd) : Co ratio allowed synthesis of a system with a high alloy formation level [12, 14]. Structural characteristics of PdCo/C are presented in Sect. 3.1. The catalytic activity increase in this system as compared to Co/C is caused by PdCo alloy formation. The analysis of data obtained using XRD demonstrates that the main phase in PtCo/C (80–90%) is the Pt_3Co with cubic lattice parameter $a = 0.3854$ nm and crystallite size up to 6 nm. The other phase components are Pt and PtCo with amorphous structure and particle size below 2 nm. According to studies performed at PtCo/C (E-TEK) [2, 22], the Pt_3Co and PtCo alloys possess the highest activity for cathodic oxygen reduction in acidic solutions. The alloy formation is also confirmed by the negative shift of the $Pt4f_{7/2}$ level in the PtCo/C system as compared to Pt/C (Fig. 2b). Thus, the alloy formation results in an increase in activity of the Pt- and Pd-based catalytic systems. In the case of PdCo/C, however, the proportion of the alloy formed does not exceed 15%.

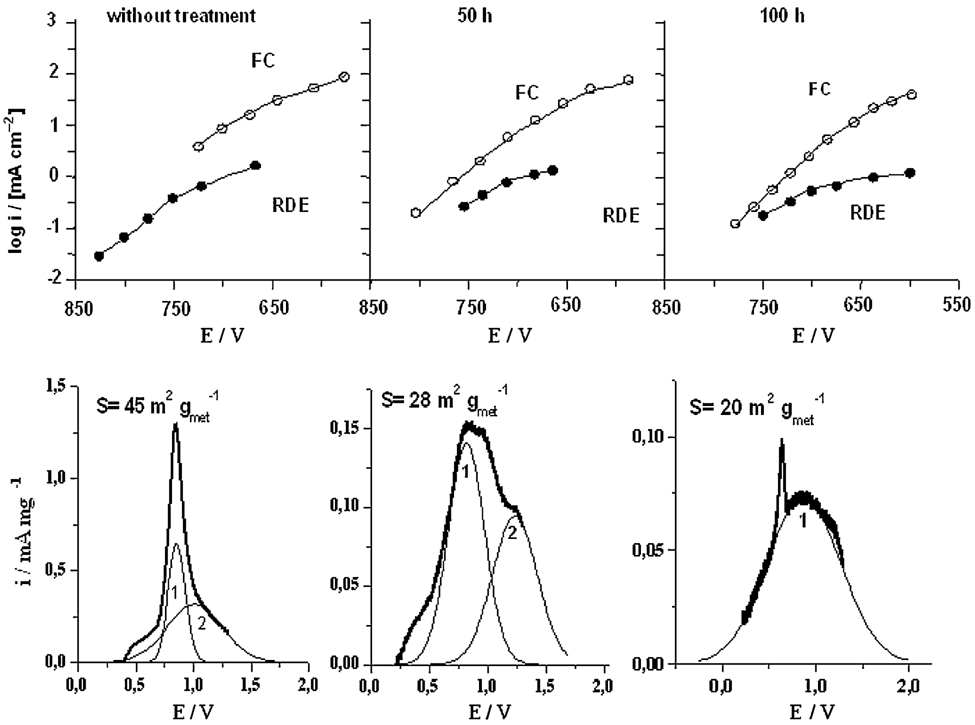
An important property of cathodic catalysts for low-temperature FC is their tolerance towards organic fuels, particularly methanol. The partial penetrability of the polymer electrolyte for alcohol (cross-over effect) results in alcohol penetration to the cathode with its further oxidation and the possibility of catalyst poisoning.

As shown earlier [23], Co and FeN_4-complexes on carbon supports obtained by pyrolysis are tolerant towards low-molecular alcohols. Electrocatalytic activity in ORR and tolerance towards methanol of the catalysts with Pd-transition metal alloys without carbon support is shown in [24].

PdCo/C catalysts (Fig. 3) show a lower activity towards ORR as compared to Pt. However, unlike Pt, methanol produces practically no effect on the oxygen electroreduction rate up to 60 °C and a concentration of 0.5 M. Table 4 shows polarization data for oxygen electroreduction obtained at a RDE coated with the Co/C and PdCo/C catalysts. The tolerance of PdCo/C catalyst towards methanol is an important advantage of this system.

The specific activity of the binary PtM systems (M = Co, Cr, Ni etc.) is higher than that of Pt catalyst per Pt weight [22, 25]. Their tolerance was confirmed by studies performed at PtCo/C (7.3 wt.% Pt). A current decrease over the whole studied range of potentials and a polarization curve shift in the cathodic direction is observed (Fig. 5, curves 1, 1′) in the presence of 0.5 M methanol. This demonstrates not only the occurrence of coupled reactions of oxygen reduction and alcohol oxidation, but also catalyst poisoning by the products of methanol oxidation.

Fig. 4 Influence of the acidic treatment time (treatment at 60 °C) on the electrocatalytic activity of the PdCo/C catalyst in ORR within the methanol–oxygen FC cathode and in model conditions (RDE) and also on the metal surface area, determined from CO desorption



The PtCo/C (7.3 wt.% Pt) catalyst was modified by phosphorus or sulfur in order to impart tolerance towards methanol. Modification of the PtCo/C catalyst results in a decrease in the metal phase specific surface area (Table 5). The modified PtCoS(Pt : S = 1 : 1) system possesses the highest surface area. The value of its specific surface area (61 m^2 g^{-1}) corresponds to the average particle size of 3–6 nm, which is in agreement with data from structural studies.

The electrocatalytic activity of the studied systems (Table 5, Figs. 5 and 6) depends on the type of precursor used during synthesis. The mechanism of O_2 electroreduction remains practically the same. This follows from the closeness of the slope values ($\partial E/\partial \log i$) of the Tafel dependences (0.060–0.075 V in the range of potentials near the steady-state potential and 0.110–0.120 V in the potential range 0.83–0.70 V). The PtCoP/C systems synthesized on the basis of $C_{18}H_{15}OP$ and PtCoS/C(Pt : S = 1 : 1) are close to the activity of PtCo/C catalyst in terms of their activity towards ORR (Table 5). Figure 6 shows the polarization curves of ORR in the presence of methanol. The activity of the PtCo/C catalyst for ORR in the presence of methanol is considerably lower (curve 1) than in the case of the P-modified systems. This is expressed in the shift of the steady-state potential (E_{st}) towards less positive values and in the decrease in oxygen reduction current. At the same time, methanol at PtCo/C is oxidized in the range of potentials corresponding to ORR. The rate of methanol oxidation in the modified systems is considerably lower and occurs at potentials more positive than 0.80 V, while the oxygen reduction current in the case of these systems is higher. This explains the decrease in oxygen reduction current at PtCo/C catalyst by the coupled methanol oxidation reaction and, possibly, surface poisoning by alcohol oxidation products. Figure 5 contains polarization curves of oxygen reduction measured at the initial PtCo/C catalyst and at the similar catalyst modified by sulfur, in the presence and absence of methanol. The tolerance of the PtCoS/C (Pt : S = 1 : 1) catalyst towards methanol is higher than in the case of the initial catalyst (Table 5, Fig. 5).

Table 4 Current density of oxygen reduction obtained at RDE in the absence and presence of 0.5 M methanol

Catalyst: XC 72 +	i/mA cm^{-2} in the absence of methanol at E/V (rhe)		i/mA cm^{-2} in the presence of 0.5 M methanol at E/V (rhe)	
	0.70	0.60	0.70	0.60
Co, 3.2 wt.%	0.26	0.90	0.28	1.02
PdCo (1 : 1), 9 wt.%	0.50	1.20	0.50	1.22

0.5 M H_2SO_4, 20 °C

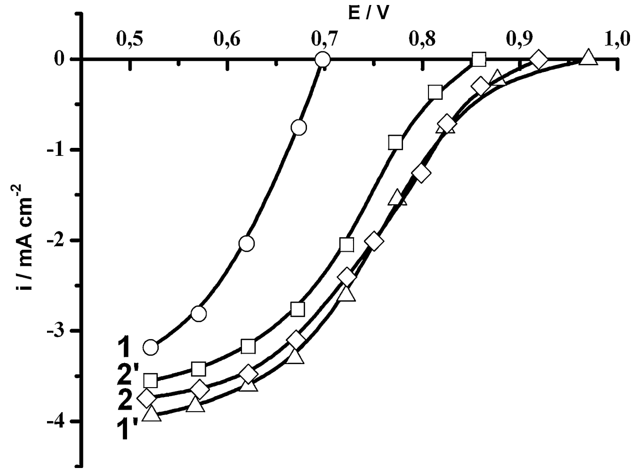


Fig. 5 Polarization curves of oxygen reduction at RDE with catalyst: (1, 1′) PtCo/C and (2, 2′) PtCoS/C(Pt : S = 1 : 1). Curves (1, 2)—in the absence of methanol, curves (1′, 2′)—in the presence of 0.5 M methanol. 0.5 M H_2SO_4; scan rate, 5 mV s^{-1}; 60 °C; the oxygen atmosphere; the electrode rotation rate, 1,420 rpm

The analysis of XPS spectra of the PtCoS/C system showed the interaction between Pt and S. This is demonstrated by the appearance of a component with a binding energy of 71.6 eV in the $Pt4f_{7/2}$ core level band and of a component with a binding energy of 161.8 eV in the $S2p_{3/2}$ core level of the sulfur band. The former corresponds to platinum in the Pt^{2+} state, while the latter is characteristic of sulfur interacting with a metal, in this case platinum.

3.3 Tests of developed cathodic catalysts in H_2–air and methanol–oxygen FC

3.3.1 Hydrogen–air FC

The successful synthesis of PdCo/C catalyst for oxygen reduction and PdRu/C catalyst for hydrogen oxidation [26] allowed study of the possibility of the development of a Pt-free hydrogen–air FC with proton–conducting electrolyte.

Pd-containing bimetallic catalysts are characterized by different morphology, hydrophilic–hydrophobic properties and a lower activity, as compared to the carbon supported Pt. Therefore, partial active layer optimization was performed. This consisted in optimization of Nafion loading in the active layer. The catalyst loading ranged within 2.5–3.5 mg cm^{-2}, while the Nafion content was 35–40 wt.%. Figure 7a shows the discharge curves measured in a prototype of a Pt-free hydrogen–air FC. It can be seen that the power density (Fig. 7b) achieved is 270 mW cm^{-2}.

3.3.2 Methanol–oxygen FC with Co-containing catalysts

No optimization of active layers (AL), GDL, or MEA was performed, as our objective was to study specific activity and tolerance of Co-containing catalysts in standard conditions.

The dependence of the methanol–oxygen FC specific power on cell voltage is shown in Fig. 8. The cells were assembled using three types of oxygen reduction catalysts, 20 wt.% Pt(E-TEK), PtCo/C, and PtCoS/C. In all cases the catalyst loading was 3 mg cm^{-2}. The employment of PtCo/C catalyst allows decreasing Pt consumption while preserving the catalyst characteristics. Complete replacement of Pt by the methanol-tolerant PdCo/C system results in a specific power decrease down to 15–20 mW cm $^{-2}$.

Tests of various Pt-containing catalysts in FC prototypes (Table 6) were performed to compare their tolerance towards methanol. The catalyst loading was chosen so that the amount of Pt in the cathodes of the three FCs was virtually the same. In all three FCs the anode was prepared using PtRu/C (E-TEK) catalyst.

In order to determine the catalyst activity in ORR, the FC was fed with hydrogen in place of methanol. As the hydrogen oxidation overpotential is much lower than the

Table 5 Effect of the precursor type on the specific surface value (S_{CO}) and activity in ORR for the studied catalysts in the absence and the presence of 0.5 M methanol

Catalyst: XC 72 + PtCo + P or S	S_{CO}/m^2 g^{-1}	E_{st}/V (rhe) in the absence of CH_3OH	i/mA cm $^{-2}$, in the absence of CH_3OH at E = 0.80 V	E_{st}/V (rhe), in the presence of CH_3OH	i/mA cm^{-2}, in the presence of CH_3OH, E = 0.65 V
Without P and S	70	0.97	1.30	0.64	0.85
P(red)	39	0.94	0.38	0.77	1.40
$C_{18}H_{15}OP$	35	0.99	1.30	0.75	1.60
$C_{18}H_{24}P_2F_6$	38	0.95	0.57	0.80	1.90
Pt/S = 1 : 0.5	58	0.87	1.20	0.82	1.80
Pt/S = 1 : 1	61	0.92	1.30	0.87	2.10
Pt/S = 1 : 2	34	0.87	0.60	0.78	1.8

0.5 M H_2SO_4, 60 °C

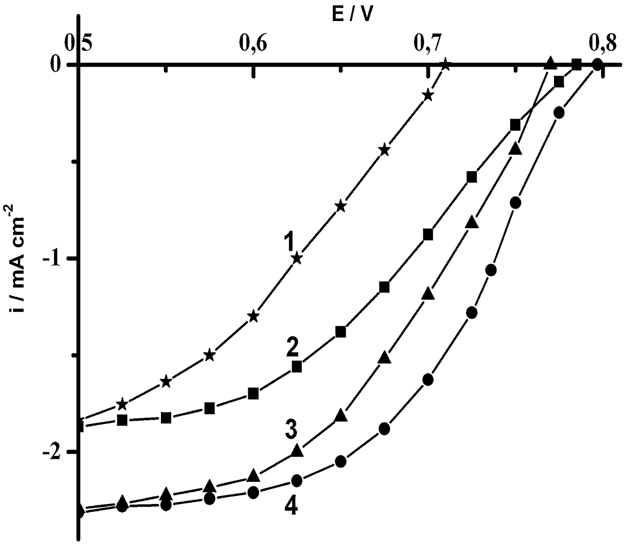


Fig. 6 Polarization curves of oxygen reduction at RDE with catalyst: (1) PtCo/C and (2–4) PtCoP/C in the presence of 0.5 M methanol. Phosphorus compounds used during the synthesis: (2) P (red); (3) $C_{18}H_{15}P$; (4) $C_{18}H_{24}P_2F_6$. 0.5 M H_2SO_4; scan rate, 5 mV s^{-1}; the electrode rotation rate, 620 rpm; 60 °C; the oxygen atmosphere

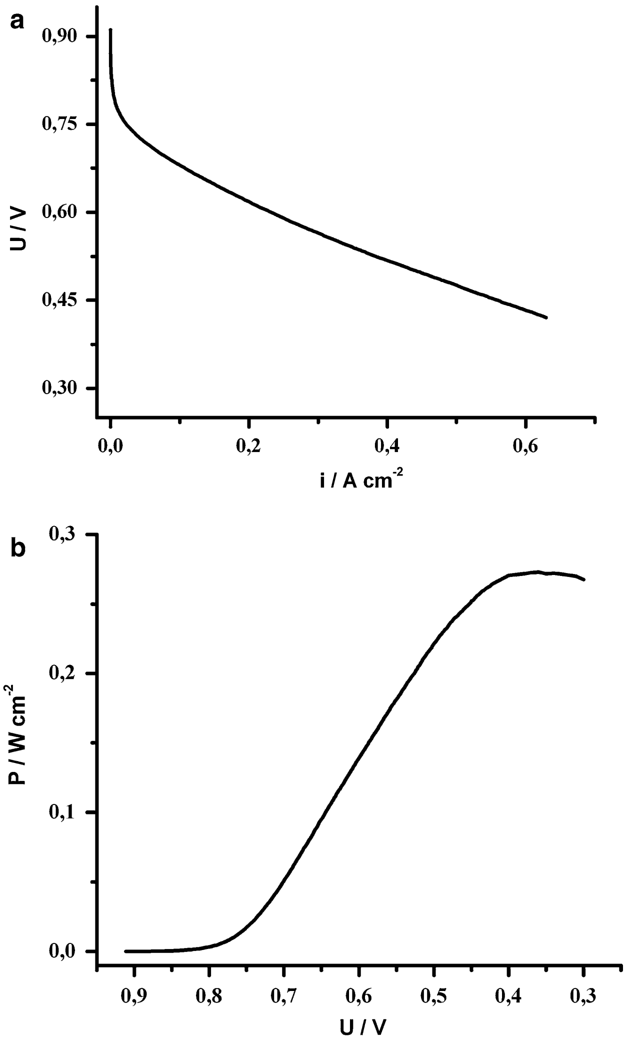


Fig. 7 Discharge curve (**a**) and power density (**b**) for hydrogen–air FC with a Nafion membrane 117 at 60 °C. Cathode–PdCo/C; anode–PdRu/C

oxygen reduction overpotential, the hydrogen electrode polarization can be neglected. Table 7 shows that the activity of cathodic catalysts decreases in the following order: PtCo/C > PtCoS/C > Pt/C. Tests of the same FCs were performed using 1 M methanol.

The curves of voltage dependence of the specific power for methanol–oxygen FC assembled using the above three cathodic catalysts are presented in Fig. 9. The maximum specific performance is achieved in the case of nonmodified PtCo/C catalyst. However, the specific performance measured at the cell voltage exceeding 0.45 V is highest for the FC with PtCoS/C oxygen reduction catalyst. This can be explained by a higher tolerance of PtCoS/C catalyst towards methanol as compared to the other catalysts tested.

To rationalize the methanol tolerance of the oxygen reduction catalyst the following experiment was devised. 1 M methanol solution was circulated through the oxygen electrode compartment while hydrogen was supplied to the anodic compartment. Methanol oxidation currents at oxygen reduction catalysts versus cell voltage in this configuration were measured (not shown). The steady-state currents of 1 M methanol oxidation at the cell voltage of 0.7 V (i_{meth}) are presented in Table 7. Since the counter electrode was a hydrogen electrode, the cell voltage is nearly equal to the methanol oxidation potential measured versus a hydrogen reference electrode. The values of these methanol oxidation currents (i_{meth}) were compared to oxygen reduction currents (i_{O_2}) measured at a cell voltage 0.7 V, when the cells were tested in the standard PEM configuration. The values ($i_{O_2}/i_{\mathrm{meth}}$) can be used as a measure of the methanol tolerance of the oxygen reduction catalyst. The catalyst activity in the methanol oxidation reaction decreases in the following order Pt/C ~ PtCo/C > PtCoS/C. As follows from the ($i_{O_2}/i_{\mathrm{meth}}$) values, the tolerance of PtCoS/C catalyst towards methanol is at least double the tolerance of PtCo/C catalyst and six times higher than that of Pt/C catalyst.

4 Conclusions

A highly dispersed nanozise cathodic PdCo/C catalyst was synthesized for the first time by means of a high-temperature thermochemical method and its structural, electrochemical and corrosion characteristics were investigated.

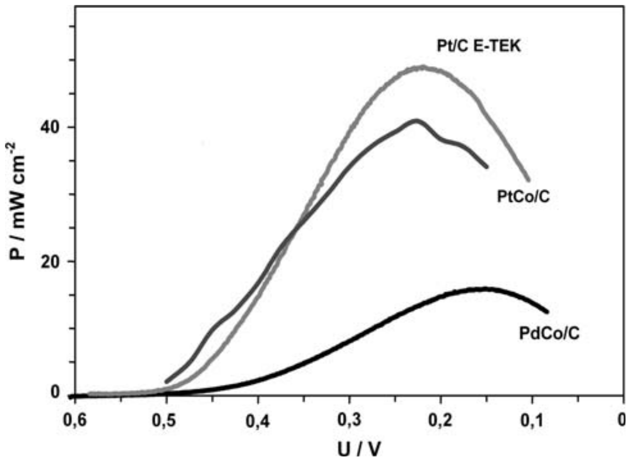


Fig. 8 Dependence of specific power density on voltage for methanol–oxygen FC with a Nafion 117 membrane and different cathodic catalysts, their content being 3 mg cm^{-2}; the anode was 30%PtRu (E-TEK) in all cases. The temperature was 50 °C

Table 6 Anodic and cathodic catalysts in the prototypes of hydrogen– and methanol–oxygen FC

Prototype	Anode mass 20 wt.%Pt + 10 wt. %Ru/mg cm^{-2}		Cathode mass/mg cm^{-2}	
	Catalyst	Pt	Catalyst	Pt
1	3.5	0.7	20 wt.%Pt (E-TEK)—1.86	0.36
2	3.5	0.7	PtCo/C—4.30	0.31
3	3.5	0.7	PtCoS/C—4.00	0.29

Table 7 Parameters of cathodic catalysts in FC prototypes at 50 °C and atmospheric oxygen pressure

Parameters at E = 0.70 V	Cathodic catalysts		
	Pt(E-TEK)	PtCo/C	PtCoS/C
i_{O_2}—O_2 reduction current density/A cm^{-2}	0.12 (1)	0.32 (2.7)	0.16 (1.3)
i_{meth}—1 M CH_3OH oxidation current density/A cm^{-2}	0.18	0.17	0.037
i_{O_2}/i_{meth}	0.66 (1)	1.8 (2.7)	4.3 (6.45)

The ratio of the measured value to the corresponding value at Pt catalyst (taken as a reference unit) is given in brackets

Good corrosion stability allowed the testing of PdCo/C electrocatalyst in the MEA of methanol–oxygen and hydrogen–air FCs. It was shown that the PdCo/C system can serve as an alternative to Pt in a number of low-temperature FC applications.

Modification of the PtCo/C (7.3%Pt) catalyst by sulfur yielded increased methanol tolerance.

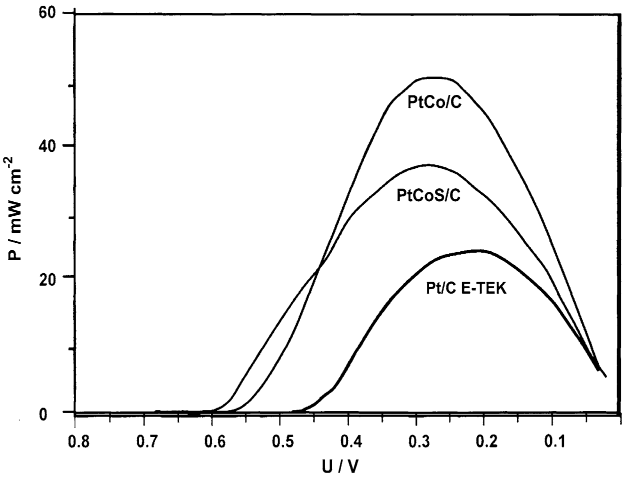


Fig. 9 Dependence of the power density on voltage for methanol–oxygen FC prototypes at 50 °C and atmospheric oxygen pressure. Pt amount at the cathode, mg cm^{-2}: 20%Pt (E-TEK), 0.36; PtCo/C, 0.29; PtCoS/C, 0.31. In all cases, the anode was PtRu/C with Pt content being 0.7 mg cm^{-2}

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